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SiALON CONTAINING YTTERBIUM AND METHOD OF MAKINGFIELD OF THE INVENTION

The invention pertains to a ceramic material,
as well as a method of making the same, that contains
5 silicon aluminum oxynitride (SiAlON) and ytterbium.

BACKGROUND OF THE INVENTION

SiAlON materials have a number of uses such
as, for example, cutting inserts for various metal
cutting application and wear parts for various wear
10 applications (e.g., plunger rods for pumps, plunger
ball blanks, down hole pump check valve blanks,
bushings, blast nozzles, and other wear and impact
applications). Exemplary patents that disclose SiAlON
materials are U.S. Patent No. 4,563,433 and U.S. Patent
15 No. 4,711,644. One article that discusses SiAlON
materials is Izhevskiy et al., "Progress in SiAlON
ceramics, Journal of the European Ceramic Society 20
(2000) pages 2275-2295.

SiAlON materials may contain an alpha prime
20 (or alpha') phase and a beta prime (or beta') phase and
one or more other phases such as, for example, a glassy
phase and/or a crystalline phase. The alpha prime
SiAlON phase may be of the formula $M_x\text{Si}_{12-(m+n)}\text{Al}_{m+n}\text{O}_n\text{N}_{16-n}$
where M is Li, Ca, Y or other lanthanides and where the
25 theoretical maximum of x is 2, the value of n ranges
between greater than 0 and less than or equal to 2.0,
and the value of m ranges between greater than or equal
to 0.9 and less than or equal to 3.5. The beta prime
SiAlON phase may be of the formula $\text{Si}_{6-z}\text{Al}_z\text{O}_z\text{N}_{8-z}$ where
30 $0 < z \leq 4.2$. In the case where M is yttrium, the
crystalline phases may include YAG (yttrium aluminum
garnet) which is a cubic phase of the formula $\text{Y}_3\text{Al}_5\text{O}_{12}$;
YAM which is a monoclinic phase of the formula $\text{Y}_4\text{Al}_2\text{O}_9$;
N-YAM which is a monoclinic phase of the formula

$Y_4Si_2O_7N_2$; and Y-N- α -Wollastonite which is a monoclinic phase of the formula $YSiO_2N$.

SiAlON materials may comprise an alpha prime SiAlON phase and a beta prime SiAlON phase, as well as
5 further contain silicon carbide particles dispersed throughout the SiAlON matrix. Such a SiAlON material is disclosed in U.S. Patent No. 4,826,791 to Mehrotra et al.

Other ceramic materials include an alpha
10 prime SiAlON phase, a beta SiAlON phase and an intergranular phase wherein the ceramic optionally contains refractory phases. The ceramic material has an alloyed surface with a higher oxygen and aluminum content. U.S. Patent No. 4,880,755 to Mehrotra et al.
15 discloses such a ceramic material.

U.S. Patent No. 5,370,716 to Mehrotra et al. discloses a high Z-SiAlON material comprising beta prime SiAlON phase. The beta prime SiAlON phase has a formula $Si_{6-z}Al_2O_2N_{8-z}$ where $1 < z < 3$.

20 U.S. Patent No. 5,908,798 to Chen et al. discloses a SiAlON material wherein the focus is on the reinforcement of alpha prime SiAlON with elongated grains of alpha prime SiAlON. The examples that include ytterbium produce a material with only alpha
25 prime SiAlON phase that does not contain any beta prime SiAlON phase.

U.S. Patent No. 6,124,225 to Tien et al. focuses upon the use of gadolinium (Gd) in a SiAlON material to produce an alpha prime SiAlON material that
30 is reinforced by elongated grains of alpha prime SiAlON.

Although current SiAlON cutting inserts exhibit acceptable properties (e.g., hardness, toughness, thermal shock resistance) it would be
35 desirable to provide for an improved SiAlON material that has application as a cutting insert that exhibits improved metal cutting performance properties including

hardness, Young's modulus, toughness, thermal conductivity, and thermal shock resistance. The same is true for SiAlON wear parts in that although current SiAlON wear parts have acceptable properties (e.g.,
5 hardness, Young's modulus, toughness, thermal conductivity, and thermal shock resistance), it would be desirable to provide an improved SiAlON material that has application as a wear part that exhibits improved properties.

10 SUMMARY OF THE INVENTION

In one form thereof, the invention is a sintered ceramic body made from a starting powder mixture that includes silicon nitride powder. Less than or equal to about 5 weight percent of the starting
15 silicon nitride powder comprises beta-silicon nitride. The ceramic body comprises a two phase composite of alpha prime SiAlON phase and beta prime SiAlON phase. The alpha prime SiAlON phase contains ytterbium therein. The alpha prime SiAlON phase is present in an
20 amount between about 25 weight percent and about 85 weight percent of the two phase composite.

In still another form thereof, the invention is a ceramic composition that comprises a two phase composite of alpha prime SiAlON phase and beta prime
25 SiAlON phase. The alpha prime SiAlON phase has ytterbium therein. The alpha prime SiAlON phase is present in an amount between about 45 weight percent and about 85 weight percent of the two phase composite. The composition further includes an intergranular
30 phase.

In another form thereof, the invention is a ceramic composition that consists essentially of an alpha prime SiAlON phase and a beta prime SiAlON phase. The alpha prime SiAlON phase has ytterbium therein.
35 The alpha prime SiAlON phase is present in an amount between about 45 weight percent and about 85 weight

percent of the total content of the alpha prime SiAlON phase and the beta prime SiAlON phase. The beta prime SiAlON phase is present in an amount between about 15 weight percent and about 55 weight percent of the total content of the alpha prime SiAlON phase and the beta prime SiAlON phase. The composition further includes an intergranular phase wherein the intergranular phase includes one or more of a glassy phase and an intergranular crystalline phase.

10 In still another form thereof, the invention is a sintered ceramic body made from a starting powder mixture wherein the starting powder mixture includes silicon nitride powder. Less than or equal to about 2 weight percent of the starting silicon nitride powder
15 comprises beta-silicon nitride. The sintered ceramic body comprises a two phase composite of an alpha prime SiAlON phase and a beta prime SiAlON phase. The alpha prime SiAlON phase has ytterbium therein. The alpha prime SiAlON phase is present in an amount greater than
20 about 25 weight percent of the two phase composite. The composition further includes an intergranular phase.

 In yet another form thereof, the invention is a ceramic composition that comprises a two phase
25 composite of an alpha prime SiAlON phase and a beta prime SiAlON phase. The alpha prime SiAlON phase has therein one or more elements selected from the group consisting of ytterbium, erbium, thulium, scandium and lutetium. The alpha prime SiAlON phase is present in
30 an amount between about 45 weight percent and about 85 weight percent of the two phase composite. The ceramic composition further includes an intergranular phase.

 In still another form thereof, the invention is a sintered ceramic body made from a starting powder
35 mixture that includes silicon nitride powder, wherein the starting silicon nitride powder comprising less than or equal to about 2 weight percent beta-silicon nitride.

The ceramic body comprises a two phase composite that includes an alpha prime SiAlON phase containing ytterbium therein and a beta prime SiAlON phase. The composition of the ceramic body falls above the line x-x in FIG. 5.

In another form thereof, the invention is a sintered ceramic body made from a starting powder mixture that includes silicon nitride powder, wherein the starting silicon nitride powder comprising less than or equal to about 5 weight percent beta-silicon nitride. The ceramic body comprises a two phase composite that includes an alpha prime SiAlON phase and a beta prime SiAlON phase. The alpha prime SiAlON phase contains one or more rare earth elements therein, and wherein for a valence of +3 and a coordination number of 6 the effective ionic radius of each one of the rare earth elements equals less than 0.900 Angstroms. The alpha prime SiAlON phase is present in an amount greater than or equal to about 25 weight percent of the two phase composite.

BRIEF DESCRIPTION OF THE DRAWINGS

The following is a brief description of the drawings that accompany and form a part of this patent application:

FIG.1 is an isometric view of a first specific embodiment of a cutting insert that does not have a coating;

FIG. 2 is an isometric view of a second specific embodiment of a cutting insert wherein the cutting insert has a coating and a part of the coating has been removed to expose the substrate;

FIG. 3 is a photomicrograph showing the microstructure of a yttrium-containing SiAlON material (Example C as described hereinafter) wherein the scale of the photomicrograph is such that it represents a 35 micron square;

FIG. 4 is a photomicrograph showing the microstructure of a ytterbium-containing SiAlON material (Example 2 as described hereinafter) that contains alpha prime SiAlON grains that are equi-axed in shape and beta prime SiAlON grains that are elongate in shape, and wherein the scale of the photomicrograph is such that it represents a 35 micron square; and

FIG. 5 is a graph showing the projection of the selected examples as designated therein (i.e., Examples 5-25 and 27-29) onto the silicon nitride corner of the base plane of a three-dimensional behavior diagram for SiAlON wherein the four corners of the base plane comprise aluminum nitride, aluminum oxide, silicon oxide and silicon nitride, and the remaining two corners of the six-cornered behavior diagram comprise one corner opposite and above the silicon nitride and aluminum nitride corners of the base plane that is ytterbium nitride and the other corner opposite and above the aluminum oxide and silicon oxide corners of the base plane that is ytterbium oxide.

DETAILED DESCRIPTION OF THE INVENTION

The invention pertains to a ceramic material, and more specifically, to a silicon aluminum oxynitride (SiAlON) material that contains ytterbium. Applicant contemplates that the SiAlON material may include one or more of erbium, thulium, scandium and/or lutetium either with or without ytterbium.

SiAlON materials have been used as cutting inserts in a variety of metal cutting applications. SiAlON materials have also been used as wear parts for various wear applications and impact parts for various impact applications. The SiAlON material of the present invention has application as a cutting insert, a wear part, an impact part, and any other article

wherein the properties of a hard dense ceramic material are desirable.

In the present invention, the SiAlON material contains an alpha prime phase of the formula $Yb_xSi_{12-(m+n)}Al_{m+n}O_nN_{16-n}$. Applicant has not determined the values of x, m, and n for the material of the present invention. However, applicant would expect the value of x to have a theoretical maximum of 2. Applicant also would expect the value of n to range between greater than 0 and less than or equal to 2.0, and the value of m to range between greater or equal to 0.9 and less than or equal to 3.5.

The alpha prime SiAlON phase comprises generally equi-axed grains. The SiAlON material also contains a beta prime phase of the formula $Si_{6-z}Al_zO_zN_{8-z}$. The preferred values for z range between greater than .3 and less than 1.5 wherein different applications have different preferred ranges of the "z" value. For example, the preferred value for z ranges between greater than .3 and less than .6 for applications in which the invention is used as a cutting tool to machine cast iron. As another example, the preferred value for z ranges between greater than .7 and less than 1.5 for applications in which the invention is used as a cutting tool to machine a high temperature alloy (e.g., Inconel 718). The beta prime SiAlON phase comprises generally elongated grains.

In one range for the alpha prime SiAlON phase content, especially when the ceramic is made from a starting powder mixture that includes silicon nitride powder wherein less than or equal to about 2 weight percent of the starting silicon nitride powder comprises beta-silicon nitride and greater than or equal to about 98 weight percent of the starting silicon nitride powder comprises alpha-silicon nitride, the alpha prime phase is present in an amount between about 25 weight percent and about 85 weight percent of

the total of the alpha prime SiAlON phase and beta prime SiAlON phase content of the SiAlON material. In another range, the alpha prime SiAlON phase is present in an amount between about 45 weight percent and about 5 85 weight percent of the total of the alpha prime SiAlON phase and beta prime phase content of the SiAlON material. In still another range, the alpha prime SiAlON phase is present in an amount between about 60 weight percent and about 80 weight percent of the total 10 of the alpha prime SiAlON phase and beta prime SiAlON phase content of the SiAlON material. The content of the alpha prime SiAlON phase is typically measured by X-ray diffraction techniques.

In one range, especially when the ceramic is 15 made from a starting powder mixture that includes silicon nitride powder wherein less than or equal to about 5 weight percent of the starting silicon nitride powder comprises beta-silicon nitride and greater than or equal to about 95 weight percent of the starting 20 silicon nitride powder comprises alpha-silicon nitride, the beta prime SiAlON phase is present in an amount between about 15 and about 75 weight percent of the total of the alpha prime SiAlON phase and beta prime SiAlON phase content of the SiAlON material. In 25 another range, the beta prime SiAlON phase is present between about 15 weight percent and about 55 weight percent of the total of the alpha prime SiAlON phase and beta prime SiAlON phase content of the SiAlON material. In still another range, the beta prime 30 SiAlON phase is present between about 20 weight percent and about 40 weight percent of the total of the alpha prime SiAlON phase and beta prime SiAlON phase content of the SiAlON material. The content of the beta prime SiAlON phase is typically measured by X-ray diffraction 35 techniques.

The SiAlON material also contains one or more additional phases including an intergranular phase.

The intergranular phase may comprise a glassy phase and an intergranular crystalline phase may sometimes also be present. At the present time, applicant is not certain of the specific amount of additional phases typically present in the SiAlON material. However, applicant estimates that the intergranular phase, which typically includes a glassy phase and possibly an intergranular crystalline phase, is present. The glassy phase is typically an amorphous phase.

10 The intergranular crystalline phases that may be present are: YbAG (ytterbium aluminum garnet) which is a cubic phase of the formula $\text{Yb}_3\text{Al}_5\text{O}_{12}$; YbAM which is a monoclinic phase of the formula $\text{Yb}_4\text{Al}_2\text{O}_9$; N-YbAM which is a monoclinic phase of the formula $\text{Yb}_4\text{Si}_2\text{O}_7\text{N}_2$.
15 The SiAlON material does not contain any intergranular crystalline phases that includes B-phase of the formula $\text{Yb}_2\text{SiAlO}_5\text{N}$ or a Wollastonite phase.

Referring to the drawings, FIG. 1 illustrates a RNG-T style of a cutting insert generally designated as 20. The cutting insert 20 has a flank surface 22 that is generally cylindrical in shape and a pair of opposite rake surfaces 24 that are each generally circular in shape. The flank surface 22 intersects with the rake surfaces 24 to define circular cutting edges 26. The cutting edge 26 has a bevel. Cutting insert 20 comprises the SiAlON material of the present invention.

FIG. 2 illustrates a second specific embodiment of a cutting insert generally designated as 30. Cutting insert 30 has a substrate 32 and a coating 34. Cutting insert 30 has a generally cylindrical flank surface 36 and a pair of opposite generally circular rake surfaces 38. The flank surface 36 intersects the rake surfaces 38 to form circular cutting edges 40. Each cutting edge 40 has a bevel. The substrate 32 comprises the SiAlON material of the present invention. The coating may include a

coating scheme of one or more layers applied by known techniques including chemical vapor deposition (CVD) and physical vapor deposition (PVD). The coating materials may include CVD-applied alumina applied to a depth of between 1 to 10 micrometers or to a more preferred depth of 3 to 5 micrometers. The coating materials may also include PVD-applied titanium aluminum nitride. The coating materials may further include multi-layer coating schemes wherein it is preferable that the layer adjacent to the substrate comprise alumina.

In the following examples, the physical properties of a yttrium-containing SiAlON material were compared to the physical properties of a ytterbium-containing SiAlON material. Table 1 sets forth starting powder compositions (in weight percent) of Batch Nos. 982 and 1030 which are ytterbium-containing materials and Batch No. 941A which is a yttrium-containing material. These compositions (i.e., Batch Nos. 982, 1030 and 941A) were made such that the molar content of the ytterbia in Batch Nos. 982 and 1030 was the same as the molar content for the yttria in Batch No. 941A. The starting powder mixture for each one of Batch Nos. 982, 1030 and 941A contained silicon nitride powder wherein about 1.6 weight percent of the starting silicon nitride powder comprised beta-silicon nitride powder and about 98.4 weight percent of the starting silicon nitride powder comprised alpha-silicon nitride.

Table 1
Starting Powder Compositions
for Batch Nos. 982, 1030 and 941A
[in weight percent]

Batch No.	Silicon Nitride [Starck M11]	Silicon Nitride [Ube SNE-03]	Aluminum Nitride [Starck Grade A]	Aluminum Oxide [Ceralox HPA-0.5]	Ytterbia [Molycorp]	Yttria
982	20.57	61.70	5.97	3.56	8.20	-
1030	21.07	63.22	6.00	1.50	8.20	-
941A	21.35	64.05	6.20	3.70	-	4.70

5 The starting powders are briefly described as follows. One of the silicon nitride powders was from Herman C. Starck of New York. New York (USA) under the designation M11. Another of the silicon nitride powders was from Ube Industries, Ltd. Of Tokyo, Japan. under
10 the designation SNE-03. The aluminum nitride was from Herman C. Starck under the designation Grade A. The aluminum oxide was from Ceralox Corporation of Tucson, Arizona (USA) under the designation HPA-0.5 (which contains a deliberate addition of 0.5 weight percent
15 magnesia). The ytterbia was from Molycorp. The yttria was a fine grade yttria available from Herman C. Starck.

Each one of the above Batch Nos. set out in Table 1, the starting composition was milled for a time
20 of between about 8 hours and about 16 hours with isopropanol and using an alpha' SiAlON-beta' SiAlON media to form a slurry. After completion of the milling, the slurry was discharged through a 400 mesh screen and then vacuum dried to form a dry powder. The
25 dry powder was then fitzmilled and pellitized using a fluid bed process. Rosin and Carbowax 400 were added as binders during the fluidization process. The pellitized material (dry powder and the binder

material) was then dry pressed into green compacts with a density of between about 2 to about 2.15 grams per cubic centimeter. The binder was then removed by an air burnout cycle that had a maximum temperature of about 875 degrees Centigrade.

These compacts were then loaded into BN (boron nitride) saggars that had dimensions of 4 inches x 8 inches x 1.25 inches. There were three layers of compacts per box with 55 compacts per layer for the RNG43 and CNGA433 style cutting inserts. The BN saggars were stacked two high and placed on the belt of a continuous sinter furnace. The furnace had four independently controlled heating zones wherein each heating zone was 12 inches long. The ramp rate for the heat up was about 150 degrees Centigrade per minute. The furnace is along the lines of the furnace described in U.S. Patent No. 5,648,042 to Miller, Jr. entitled HIGH TEMPERATURE BELT FURNACE APPARATUS AND METHOD OF USING THE SAME, except that the furnace used in these examples had four heating zones.

The use of a belt furnace to sinter a compact is disclosed in Wittmer et al., "Economic Comparison of Continuous and Batch Sintering of Silicon Nitride", American Ceramic Society Bulletin, Vol. 72, No. 6 (1993), pp. 129-137; Wittmer et al., Comparison of Continuous Sintering to Batch Sintering of Si_3N_4 ", Ceramic Bulletin, Vol. 70, No. 9 (1991) pp. 1519-1527; and Wittmer et al., "Continuous Sintering of Si_3N_4 in a Controlled Atmosphere Belt Furnace". Published PCT Patent Application No. PCT/US99/14231 with an International Filing Date of June 23, 1999 for a CERAMIC AND PROCESS FOR THE CONTINUOUS SINTERING THEREOF discloses the continuous sintering in a belt furnace of a ceramic wherein the sintered product includes an alpha'-SiAlON phase and a beta'-SiAlON phase.

As shown in Table 2, each one of the Batch Nos. 982, 1030 and 941A was continuously sintered in two different ways. In this regard, Table 2 below sets forth the sintering parameters for Examples 1 through 4 (that contain ytterbium) and Examples A and B (that do not contain ytterbium). For each heating zone, Table 2 sets forth the temperature (degrees Centigrade) to which the compacts are exposed during the continuous sintering treatment. The compacts spent about 30 minutes in each one of the heating zones.

Table 2
Sintering Parameters for Examples 1-4 and A and B

Example/Batch No.	Heating Zone 1	Heating Zone 2	Heating Zone 3	Heating Zone 4
1/982 [Invention]	1770	1770	1770	1770
2/1030 [Invention]	1765	1765	1765	1765
3/1030 [Invention]	1550	1700	1765	1765
4/982 [Invention]	1550	1700	1765	1765
A/941A [Comparative]	1770	1770	1770	1770
B/941A [Comparative]	1550	1700	1765	1765

Table 3 below sets forth the phases present and the physical properties for each of the examples. The Vickers hardness (Hvn) was measured using a 18.5 kilogram load and is set forth in gigapacals. The fracture toughness (K_{IC}) was measured on a polished surface employing a Palmqvist indentation technique using a 18.5 kg load on a Vickers indenter per the article by Evans and Charles, "Fracture Toughness Determination by Indentation", J. American Ceramic Society, Vol. 59, Nos. 7-8, pages 371-372. As set forth in Table 3, the weight percent of the alpha prime SiALON phase and the beta prime SiALON phase is of the total of the alpha prime SiALON phase and the beta prime SiALON phase.

Table 3. Phases Present and Physical Properties of Examples 1-4, A and B

Example	α' - SiAlON [Weight Percent]	β' - SiAlON [Weight Percent]	Glassy Phase	Crystalline Phase [B-phase] Present [Relative Intensity]	Hvn (Gpa)	K _{IC} (MPa m ^{1/2})
1	47.0	53			18.80	7.14
2	54.2	45.8			19.78	7.23
3	57.2	42.8			19.99	7.03
4	49.7	50.3			19.24	6.72
A	42.3	57.7		6.3	18.88	5.23
B	45.0	55		1.9	18.15	6.06

The data set forth in Table 3 above shows that ytterbium-containing SiAlON materials (Examples 1-4) exhibited a higher hardness and increased toughness than did the yttria-containing SiAlON materials (Examples A and B). The absence of any B-phase or any Wollastonite crystalline phase in the ytterbium-containing SiAlON materials most likely made a contribution to the higher toughness. It would also seem like the smaller ionic radius of ytterbia as compared to yttria may lead to an improvement in the resistance to the formation of B-phase and/or Wollastonite during sintering. The yttria-containing examples (Examples A and B) each contained B-phase ($\text{Yb}_2\text{SiAlO}_5\text{N}$) as shown in Table 3.

FIG. 3 is a photomicrograph of the microstructure of Example C [Batch No. 941A continuously sintered at 1765 degrees Centigrade for 120 minutes] and FIG. 4 is a photomicrograph of the microstructure of Example 2 [Batch No. 982 continuously sintered at 1765 degrees Centigrade for 120 minutes]. In FIG. 4 the dark prismatic grains are beta prime SiAlON phase while the lighter gray grains are the alpha prime SiAlON phase. The brightest areas are a ytterbia-alumina-silica glassy phase.

As shown by Examples 1-4, applicant has found that the present invention produces a ceramic that has an alpha prime SiAlON and a beta prime SiAlON phase

wherein the ceramic has a high fracture toughness (e.g., a K_{IC} of greater than or equal to 6.0 MPam^{3/2}, and more preferably, a K_{IC} of greater than or equal to 6.5 MPam^{3/2}) together with an alpha prime SiAlON phase
5 content of greater than or equal to about 45 weight percent of the sum of the alpha prime SiAlON phase and the beta prime SiAlON phase.

Applicant has also found that the amount of the beta silicon nitride in the starting silicon
10 nitride powder has an impact upon the amount of the alpha prime SiAlON phase present in the as-sintered microstructure. More specifically, as the amount of beta silicon nitride in the starting silicon nitride powder increases, the amount of alpha SiAlON in the as-
15 sintered microstructure decreases. Applicant further believes that the higher toughness is obtained when the beta silicon nitride content in the starting silicon nitride powder is less than or equal to about 5 weight percent, and more preferably less than or equal to
20 about 2 weight percent, of the starting silicon nitride powder. In regard to each one of Examples 1-4, the content of the beta-silicon nitride in the starting silicon nitride powder mixture was about 1.6 weight percent and the content of the alpha-silicon nitride in
25 the starting silicon nitride powder was about 98.4 weight percent.

The amount of beta silicon nitride in the starting powder mixture may be controlled in one of two ways. One way is to blend predetermined amounts of two
30 or more silicon nitride powders wherein the alpha and beta contents of each powder is known so as to achieve a silicon nitride powder of a known beta content. The other way is to take 100 percent alpha silicon nitride powder and add a selected amount of 100 percent beta
35 silicon nitride powder to it to achieve a silicon nitride powder of a known beta content. This latter

way facilitates control of the particle size of the beta silicon nitride component.

While applicant does not intend to be restricted by any particular theory, applicant believes
5 that the beta silicon nitride particles are seeds for the nucleation and growth of the beta prime SiAlON grains. As the number of the beta silicon nitride particles increase the beta prime SiAlON grains impinge each other sooner so as to limit the formation of high
10 aspect ratio beta prime SiAlON grains. In addition, as the number of the beta silicon nitride particles increases the content of the alpha prime SiAlON grains decreases. The use of fewer beta silicon nitride particles in the starting powder mixture results in a
15 limited number of nucleation sites for the beta prime SiAlON grains to grow into the alpha prime SiAlON matrix during sintering. This results in beta prime SiAlON grains with a higher aspect ratio which causes a toughening of the alpha prima SiAlON phase matrix.

20 Examples 5 through 13 were produced to show the influence of the beta silicon nitride content in the starting powder on the properties of the SiAlON material. Table 4 below presents the composition of the starting powder mixtures in weight percent.

Table 4
Starting Powder Composition for Examples 5 through 13

Example/ Batch No.	Silicon Nitride (wt%)	*beta- Silicon Nitride (wt%)	Aluminum nitride (wt%)	Alumina (wt%)	Ytterbia (wt%)
5/1166D	84.3	0	6.00	1.50	8.20
6/1030	84.3	1.6	6.00	1.50	8.20
7/1145C	84.3	8	6.00	1.50	8.20
8/1374D	82.27	0	5.97	3.56	8.20
9/982	82.27	1.6	5.97	3.56	8.20
10/1145B	82.27	2	5.97	3.56	8.20
11/1145A	82.27	8	5.97	3.56	8.20
12/1196B	84.3	1.6	6.00	1.50	8.20
13/1166C	84.3	0	6.00	1.50	8.20

* Weight percent of the starting silicon nitride that comprised beta-silicon nitride and the balance of the silicon nitride powder comprised alpha silicon nitride and impurities.

The above starting powders were processed in a fashion like the processing of the starting powders of Batch No. 982. Properties of the milled powder mixture are set forth in Table 5 below.

Table 5
Starting Powder Composition for Examples 5 through 13

Example/ Batch No.	BET [m ² /gram]	Oxygen (wt %)	10%< Particle Size Distribution	50%< Particle Size Distribution	90%< Particle Size Distribution
5/1166D	4.92	2.76	0.32	0.75	1.48
6/1030	6.67	2.93	0.3	0.76	1.58
7/1145	13.4	3.25	0.21	0.52	1.31
8/1374D	4.71	3.87	0.38	0.91	1.69
9/982	6.9	3.96	0.28	0.72	1.52
10/1145B	11	4.07	0.23	0.58	1.51
11/1145A	13.4	4.26	0.23	0.55	1.28
12/1196B	7.16	3.1	0.3	0.77	1.67
13/1166C	4.92	2.76	0.32	0.75	1.48

Table 6 below sets forth the temperature for each one of the four heating zones in the furnace in degrees Centigrade. The compacts spent about 30 minutes in each one of the heating zones. Table 6 also sets forth the weight percent of the alpha prime SiAlON phase in the as-sintered material as compared to the sum of the alpha prime SiAlON phase and the beta prime SiAlON phase wherein the beta prime SiAlON phase comprises the remainder of the crystalline phases. The hardness is set forth in Vickers hardness (H_{VN}) and the fracture toughness (K_{IC}) is set forth in MPam^{1/2}.

Table 6
Heat Treating Parameters, Alpha Prime SiAlON Content,
Hardness and Fracture Toughness for Examples 5-13

Example/Batch No./wt.% beta Silicon Nitride	Zone 1 (°C)	Zone 2 (°C)	Zone 3 (°C)	Zone 4 (°C)	wt% α' - SiAlON *	Hvn (GPa)	KIC (MPa m ^{1/2})
5/1166D/0%	1550	1700	1765	1765	83.9	20.31	6.40
6/1030/1.6%	1550	1700	1765	1765	57.2	19.08	7.28
7/1145C/8%	1550	1700	1765	1765	NA [not analyzed]	18.25	5.54
8/1374D/0%	1550	1700	1765	1765	65.5	18.63	6.84
9/982/1.6%	1550	1700	1765	1765	49.7	19.24	6.96
10/1145B/2%	1550	1700	1765	1765	45	18.69	6.65
11/1145A/8%	1550	1700	1765	1765	37.7	18.11	6.00
12/1196B/1.6%	1550	1700	1800	1800	61.6	18.28	8.19
13/1166C/0%	1550	1700	1800	1800	78	19.31	7.59

* The remainder of the crystalline phases comprised beta prime SiAlON
5 phase.

The results in Table 6 show that the fracture
toughness (K_{IC}) of Examples 5 through 7, 12 and 13 were
the highest when the beta-silicon nitride content of
the starting silicon nitride powder was 1.6 weight
10 percent. In this regard, Example 6 has a fracture
toughness (K_{IC}) equal to 7.28 MPa m^{1/2}. The same was
true for Examples 9 through 11 in that the fracture
toughness was the greatest for the example (i.e.,
Example 9) that had a beta-silicon nitride content in
15 the starting silicon nitride powder equal to 1.6 weight
percent.

The results set forth in Tables 4 through 6 show that by controlling the content of the beta-silicon nitride in the starting silicon nitride powder, one can control the content of the alpha prime SiAlON phase in the as-sintered ceramic SiAlON material even though the overall composition of the starting powders (i.e., the content of the silicon nitride [alpha-silicon nitride and beta-silicon nitride], aluminum nitride, alumina and ytterbia) remains the same.

More specifically, the overall composition of the starting powders of Examples 5 and 6 was the same in that it comprised 84.3 weight percent silicon nitride (alpha-silicon nitride and beta-silicon nitride), 6.00 weight percent aluminum nitride, 1.50 weight percent alumina, and 8.20 weight percent ytterbia. Examples 5 and 6 were processed the same.

The difference between Examples 5 and 6 was in the weight percent of the starting silicon nitride powder that comprised beta-silicon nitride. In this regard, Examples 5 and 6 contained 0 weight percent and 1.6 weight percent of beta-silicon nitride, respectively, with the balance of the starting silicon nitride powder comprising alpha-silicon nitride.

Table 6 shows that the crystalline phases of the as-sintered ceramic material of Examples 5 and 6 contained 83.9 weight percent alpha prime SiAlON and 57.2 weight percent alpha prime SiAlON, respectively, with the balance comprising beta prime SiAlON phase. Examples 5 and 6 show that even though the overall compositions and the processing were the same, by controlling the amount of beta-silicon nitride in the silicon nitride starting powder, one can control the content of the alpha prime SiAlON phase in the as-sintered ceramic material.

The same relationship held true for Examples 8, 9, 10 and 11 wherein each one of these examples had the same overall composition of: 82.27 weight percent

silicon nitride (alpha-silicon nitride and beta-silicon nitride), 5.97 weight percent aluminum nitride, 3.56 weight percent alumina, and 8.2 weight percent ytterbia. Yet, the starting silicon nitride powder for
5 Examples 8, 9, 10 and 11 contained 0 weight percent, 1.6 weight percent, 2 weight percent, and 8 weight percent, respectively.

Table 6 shows that the crystalline phases of Examples 8, 9, 10 and 11 comprised 65.5 weight percent,
10 49.7 weight percent, 45 weight percent and 37.7 weight percent alpha prime SiAlON phase, respectively, with the balance comprising beta prime SiAlON phase. Like for the above Examples 5 and 6, these examples show that even though the overall starting powder
15 compositions and the processing were the same, by controlling the amount of beta-silicon nitride in the silicon nitride starting powder, one can control the content of the alpha prime SiAlON phase in the as-sintered ceramic material.

20 The same relationship held true for Examples 12 and 13 wherein each one of these examples had the same overall composition of: 84.3 weight percent silicon nitride (alpha-silicon nitride and beta-silicon nitride), 6.00 weight percent aluminum
25 nitride, 1.50 weight percent alumina, and 8.20 weight percent ytterbia. Yet, the starting silicon nitride powder for Examples 12 and 13 contained 1.6 weight percent and 0 percent, respectively.

Table 6 shows that the crystalline phases of Examples 12 and 13 comprised 61.6 weight percent and 78
30 weight percent alpha prime SiAlON phase, respectively, with the balance comprising beta prime SiAlON phase. These examples show that even though the overall starting powder compositions and the processing were
35 the same, by controlling the amount of beta-silicon nitride in the silicon nitride starting powder, one can

control the content of the alpha prime SiAlON phase in the as-sintered ceramic material.

For wear applications, it is preferable that the beta-silicon nitride content of the starting
5 silicon nitride powder comprises an amount greater than or equal to 0 weight percent and less than or equal to 2 weight percent and the alpha-silicon nitride content comprises an amount greater than or equal to 98 weight percent and less than or equal to 100 weight percent.
10 For cutting tool applications, it is preferable that the beta-silicon nitride content of the starting silicon nitride powder comprise an amount greater than 0 and less than 2 weight percent and the alpha-silicon nitride content comprises an amount greater than 98 and
15 less than 100 weight percent.

The examples also show that the alpha prime SiAlON content is the highest in the examples with zero weight percent beta silicon nitride in the starting silicon nitride powder. More specifically, Examples 5,
20 8 and 13 had an alpha prime SiAlON phase content of 83.9 weight percent, 65.5 weight percent, and 78 weight percent, respectively. The compositions with the higher alpha prime SiAlON contents had fracture toughnesses greater than the examples wherein the
25 starting silicon nitride powders contained 8 weight percent beta silicon nitride and 92 weight percent alpha silicon nitride. Example 5 was the composition with the highest alpha prime SiAlON content (83.9 weight percent) and also had the highest hardness
30 (20.31 Hvn).

Examples 14 through 19 were prepared to determine the physical properties of certain compositions. Examples 14 through 18 were prepared
35 with 0 weight percent beta silicon nitride in the starting silicon nitride powder (which means that the starting silicon nitride powder comprised about 100 weight percent alpha silicon nitride) so as to maximize

the alpha prime SiAlON content in the sintered body for each composition. Example 19 was made from a powder mixture that contained silicon nitride powder comprising about 2 weight percent beta-silicon nitride and about 98 weight percent alpha-silicon nitride. Table 7 below sets forth the compositions of the starting powder mixture for Examples 14 through 19. Batch No. 1145D (Example 19) is a comparative example and is of the same composition as Batch No. 1197G (Example 18), except that all of the silicon nitride in Batch No. 1145D (Example 19) was SNE-10 silicon nitride from Ube Industries.

The continuous sintering parameters and the hardness and fracture toughness are set forth in Table 8 for Examples 14 through 19. Examples 15 and 16, each of which had a lower rare earth content, were HIPed (hot isostatically pressed) after completion of the continuous sintering process. The maximum HIP temperature was 1830 degrees Centigrade for 30 minutes at a total pressure of 20,000 psi wherein 150 psi was nitrogen and the balance was argon.

Table 7
Starting Powder Composition for Examples 14 through 19

Example/ Batch No.	Silicon Nitride (wt%)	*beta- Silicon Nitride (wt%)	Aluminum nitride (wt%)	Alumina (wt%)	Ytterbia (wt%)
14/1197A	80.8	0	5.2	5.8	8.20
15/1197D	85.3	0	4.8	3.7	6.2
16/1197F	79.3	0	7.5	7.0	6.2
17/1417A	77.90	0	7.6	6.3	8.2
18/1197G	79.8	0	9.0	3.0	8.20
19/1145D	79.8	2	9.0	3.0	8.20

5 * Weight percent of the starting silicon nitride powder that comprised beta silicon nitride and the balance of the silicon nitride powder was alpha silicon nitride and impurities.

Table 8

Sintering Parameters and Physical Properties of Examples 14-19

Example	Composition [Batch No.]/Wt.% Beta silicon nitride	Sintering Parameters	Hardness [Hvn Gpa]	Fracture Toughness [K_{Ic} Mpa m ^{1/2}]	W/o alpha' SiALON
14	1197A/0%	1550/1700/1800/1800 @ 30 minutes per heating zone	17.52	6.12	33.5
15	1197D/0%	1550/1700/1800/1800 @ 30 minutes per heating zone	19.08	6.91	34.8
16	1197F/0%	1550/1700/1800/1800 @ 17 minutes per heating zone	18.63	6.12	42.8
17	1417A/0%	1550/1700/1765/1765 @ 30 minutes per heating zone	19.79	6.39	58.3
18	1197G/0%	1550/1700/1765/1765 @ 30 minutes per heating zone	19.16	6.15	83.4
18a	1197G/0%	1550/1700/1800/1800 @ 30 minutes per heating zone	19.21	6.66	84.1
19	1145D/2%	1765/1765/1765/1765 @ 30 minutes per heating zone			75.2

Table 8 above sets forth the sintering temperatures (degrees Centigrade) in each one of the four heating zones and the duration (minutes) the compact is in each one of the heating zones. Table 8 also sets forth the Vickers Hardness (Hvn) in gigapascals (GPa) and the fracture toughness (K_{Ic}) in MPa m^{1/2}. Table 8 also sets forth the content of the alpha prime SiALON phase in weight percent of the total of the alpha prime SiALON phase and the beta prime SiALON phase wherein the remainder of the crystalline phases comprised beta prime SiALON phase.

Examples 14 and 15 as set forth in Tables 7 and 8 each contained 0 weight percent beta-silicon nitride in the silicon nitride starting powder. Although other examples were not prepared and analyzed, applicant would expect that samples of same overall starting powder composition as Example 14 (80.8 weight percent [alpha-silicon nitride and beta-silicon nitride], 5.2 weight percent aluminum nitride, 5.8 weight percent alumina, and 8.20 weight percent ytterbia) and Example 15 (85.3 weight percent [alpha-silicon nitride and beta-silicon nitride], 4.8 weight percent aluminum nitride, 3.7 weight percent alumina, and 6.2 weight percent ytterbia), but wherein the starting silicon nitride powder would contain greater than about 5 weight percent (i.e., about 6 weight percent to about 7 weight percent) beta-silicon nitride, would produce as-sintered ceramic material that would contain about 100 weight percent beta prime SiAlON phase as the crystalline phase. In light of such an expectation, it would seem that Examples 14 and 15 also surprisingly show that one can control the content of the alpha prime SiAlON phase in the as-sintered SiAlON ceramic material by controlling the content of the beta-silicon nitride in the silicon nitride starting powder to produce alpha prime SiAlON compositions which in the past those of ordinary skill in the art would have expected to have produced compositions of only beta prime SiAlON phase.

Referring to FIG. 5, as described earlier herein, this drawing is a graph of the silicon nitride corner of the base plane of a three-dimensional behavior diagram for SiAlON. Heretofore, those of ordinary skill in the art would have expected compositions falling within the region above the line x-x to comprise about 100 weight percent beta prime SiAlON phase and intergranular phase, and those falling below the line x-x to comprise alpha prime SiAlON

phase, beta prime SiAlON phase and intergranular phase when using conventional starting silicon nitride powders containing greater than 2 weight percent beta-silicon nitride. Surprisingly, as shown in FIG. 5, Examples 14 and 15 are in a region (i.e., an oxygen-rich region) above the line x-x of FIG. 5 in which one of ordinary skill in the art would have expected to form only beta prime SiAlON phase using conventional starting silicon nitride powders containing greater than 2 weight percent beta-silicon nitride. This is contrast to a region below the line x-x of FIG. 5 where one of ordinary skill in the art would have expected to produce both alpha prime SiAlON phase and beta prime SiAlON using past practices.

Erosion tests were conducted on certain examples of the inventive ceramic, i.e., Examples 20 through 25 and certain comparative examples, Examples D-1 through D-3. The erosion tests were performed along the guidelines set forth in ASTM Procedure G76-83 (Reapproved 1989) entitled "Standard Practice for Conducting Erosion Tests by Solid Particle Impingement Using Gas Jets". The erosion testing was performed using a Pennwalt/S.S. White Airabrasive Jet Machining Unit - Model H the following parameters:

(a) the abrasive was S.S. White Accucut Abrasive that was a 50 mesh silicon carbide particle; (b) the flow rate was 6 grams per minute under a pressure of 40 pounds per square inch; (c) the nozzle (which was made of ROCTEC 100 [a fine grained tungsten carbide with dimolybdenum carbide]) was 2 inches in length with a 0.175 inch outside diameter and a 0.055 inside diameter; and (d) the nozzle position was at an angle of 90 degrees to the surface of the sample wherein the sample surface was prepared by grinding parallel using a 320 grit diamond wheel.

Examples 20 through 22 comprised Batch 1030 processed like Example 3 set forth in Table 2 hereof so

as to present physical properties and a microstructure like Example 3. Examples 23-25 comprised Batch 982 processed like Example 4 set forth in Table 2 hereof so as to present physical properties and a microstructure like Example 4. Examples D-1 through D-3 comprised a ceramic material sold by Kennametal Inc. of Latrobe, Pennsylvania, (USA) under the designation KYON 2000. KYON 2000 is an alpha prime SiAlON-beta prime SiAlON material that contains yttrium. Each one of Examples D-1 through D-3 had a composition the same as Batch No. 941A and was processed by a batch sintering technique.

Table 9 sets forth the density of the material in grams per cubic centimeter and the results of the erosion tests. The column identified as "Erosion" presents the volume loss of material (cubic centimeters) divided by the total mass (grams) of the abrasive particles that impacted the test specimen. A smaller erosion number represents a greater resistance to erosion.

Table 9

Erosion Test Results for Examples 20-25 and D-1 through D-3

Example/Batch No.	Density (g/cc)	Erosion [cm ³ /g]
20/1030	3.3524	6.57E-05
21/1030	3.3553	6.09E-05
22/1030	3.3512	7.16E-05
23/982	3.3461	7.95E-05
24/982	3.3447	6.70E-05
25/982	3.3465	7.94E-05
D-1	3.2414	1.17E-04
D-2	3.2392	1.33E-04
D-3	3.2392	1.35E-04

These erosion test results show that the inventive examples, Examples 20 through 25, have a better erosion resistance than do comparative Examples D-1 through D-3.

5 Examples 27 through 30 were analyzed by x-ray diffraction to determine the lattice parameters. Table 10 sets forth the Example No., Batch No., and values of the "a" unit cell dimension and "c" unit cell dimension, as well as the margin of error thereof in parenthesis, for the alpha prime SiAlON phase and beta prime SiAlON phase of Examples 27 through 30. The values of the unit cell dimensions were obtained according to the method described below.

Table 10

15 "a" and "c" Unit Cell Dimensions for Examples 27-30

Example/ Batch No.	"a" α' - SiAlON	"c" α' - SiAlON	"a" β' - SiAlON	"c" β' - SiAlON
27/1166C	7.78461 (.00296)	5.65844 (.00148)	7.61649 (.00472)	2.91717 (.00210)
28/1030 [1227C]	7.78787 (.00179)	5.66336 (.00091)	7.61648 (.00043)	2.91663 (.00011)
29/1166D	7.78950 (.00544)	5.67139 (.00336)	7.61659 (.00380)	2.91514 (.00271)
30/1197F	7.80527 (.00290)	5.68446 (.00236)	7.63024 (.00191)	2.93135 (.00264)

The samples were in powder form and were prepared for analysis by adding a small amount of NIST (National Institute of Standards and Testing) silicon metal powder. The NIST silicon metal powder is a certified standard material that is used to correct the peak position calculations for errors in instrument alignment. This powder blend, i.e., the powder blend

of the sample powder and the NIST silicon metal powder, was mixed with an organic binder and acetone to form a slurry. The resulting slurry was affixed to a glass slide and then allowed to dry.

5 Diffraction data was collected using standard Braggs optics minimized for peak resolution. Data was collected using as a minimum a 0.008 degrees step in the range of 75 degrees to 135 degrees. These step positions were selected so as to maximum the accuracy of the peak position determination. Data was collected for four seconds at each step. Collected diffraction data was first corrected for instrument error using the NIST silicon reference pattern. Precise diffraction peak positions were determined by fitting a pseudo-
10 Voight function to the collected data. Lattice parameters for each of the SiAlON phases were determined from the peak positions by using a "least squares" method. The resultant parameter errors are set forth in parenthesis for the alpha prime SiAlON phase and the beta prime SiAlON phase of each example.
15
20

Referring back to the values set forth in Table 10, for the alpha prime SiAlON phase the ratio of c/a , i.e., the ratio of the "c" unit cell dimension and the "a" unit cell dimension, ranges between about .726 and about .729, and more broadly between about .725 and about .730. More specifically, taking into consideration the minimum values and maximum values of the "a" and "c" unit cell dimensions, Table 11 below presents the maximum and minimum values for the c/a ratio of the alpha prime SiAlON phase of Examples 27-30.
25
30

Table 11
Minimum and Maximum Values of c/a ratio
of the Alpha Prime SiAlON Phase
for Examples 27-30

Example/Batch No.	Minimum Value of c/a Ratio	Maximum Value of c/a Ratio
27/1166C	.7264	.7273
28/1227C [1030]	.7269	.7275
29/1166D	.7271	.7290
30/1197F	.7277	.7289

5 For Examples 27-30, Table 12 sets forth the z values for the beta prime SiAlON phase wherein the z values were calculated using the following formulas:

$$z_a = a - 7.60442/0.03$$

$$z_c = c - 2.90751/0.027$$

10 $z_{c/a} = (c/a - 0.38226)/0.002$

Table 12
z Values for Examples 27-30

Example	z_a	z_c	$z_{c/a}$
27/1166C	0.402	0.358	0.374
28/1227C [1030]	0.402	0.338	0.338
29/1166D	0.406	0.331	0.323
30/1197F	0.861	0.883	0.958

Applicant contemplates that the ceramic material may optionally include hard phase particles

wherein these hard phase particles are present in an amount no greater than about 40 volume percent and no less than about 10 volume percent. Exemplary hard particles are titanium nitride, titanium carbonitride, titanium carbide, titanium boride, hafnium nitride, hafnium carbonitride, hafnium carbide, hafnium boride, zirconium nitride, zirconium carbonitride, zirconium carbide, and zirconium boride. Titanium carbonitride is the preferred hard phase particle.

Although the examples set forth herein use ytterbium, applicant contemplates that the ceramic material may utilize other rare earth components. More specifically, applicant contemplates that any one of either erbium (Er), thulium (Tm), scandium (Sc) or lutetium (Lu) may be substituted for ytterbium in the ceramic material because of their low effective ionic radii. Like ytterbium, the use of these elements (i.e., erbium, thulium, scandium or lutetium) is also likely to avoid the formation of brittle intergranular phases. The effective ionic radii of these ions for a valence of +3 and a coordination number of 6 is as follows: erbium equals 0.890 Angstroms; thulium equals 0.880 Angstroms; ytterbium equals 0.868 Angstroms; lutetium equals 0.861 Angstroms; and scandium equals 0.745 Angstroms. In contrast, yttrium has an ionic radius equal to 0.900 Angstroms [see CRC Handbook of Chemistry and Physics, 79th Edition (1998) Table 14 on page 4-121]. Typically, erbium, thulium, scandium or lutetium would be added as an oxide in the starting powder mixture. Further, applicant contemplates that the ceramic may contain a combination of two or more of ytterbium, erbium, thulium, scandium and/or lutetium.

It is apparent that the present invention provides a ceramic material, and in particular a SiALON material, that exhibits improved properties so that this material is suitable for use as a cutting insert for metal cutting application, as well as use as a wear

part (e.g., plunger rods for pumps, plunger ball blanks, down hole pump check valve blanks, bushings, blast nozzles, and other wear and impact applications).

5 The patents, patent applications, and other documents identified herein are hereby incorporated by reference herein.

Other embodiments of the invention will be apparent to those skilled in the art from a consideration of the specification of the practice of
10 the invention disclosed herein. It is intended that the specification and examples be considered as illustrative only, and that the true spirit and scope of the invention being indicated by the following claims.